**LASER INFRARED DESORPTION SPECTROSCOPY TO DETECT COMPLEX ORGANIC MOLECULES ON ICY PLANETARY SURFACES.**

L. S. Sollit[1], and L. W. Beegle[2], [1]Northrop Grumman Space Technology (One Space Park, R1/1132D, Redondo Beach, CA 90278, Luke.Sollitt@ngc.com), [2]California Institute of Technology/Jet Propulsion Laboratory (M/S 183-601 4800 Oak Grove Dr., Pasadena, California 91109, Luther.Beegle@jpl.nasa.gov).

Introduction: Laser Desorption-Infrared Spectroscopy (LD-IR) uses an IR laser pulse to desorb surface materials while a spectrometer measures the emission spectrum of the desorbed materials (Figure 1). In this example, laser desorption operates by having the incident laser energy absorbed by near surface material (~10 microns in depth). This desorption produces a plume that exists in an excited state at elevated temperatures. A natural analog for this phenomenon can be observed when comets approach the sun and become active and individual molecular emission spectra can be observed in the IR [1,2,3,4,5]. When this occurs in comets, the same species that initially emit radiation down to the ground state are free to absorb it, reducing the amount of detectable emission features. The nature of our technique results in absorption not occuring, because the laser pulse could easily be moved away form the initial desorption plume, and still have better spatial resolution then reflectance spectroscopy. In reflectance spectrscopy, trace components have a relatively weak signal when compared to the entire active nature of the surface. With LDIR, the emission spectrum is used to identify and analyze surface materials.

Potential uses: The satellites in the outer solar system include targets of high scientific interest, as described in the NRC decadal survey [6]. A future landed package on Europa will most likely be a stationary lander/penetrator, though a rover is also possible. A system capable of composition measurements of organics (and other materials) at standoff distances not accessible to any other lander sample acquisition hardware would be a valuable addition to that payload. For instance, a Titan Explorer would be an atmospheric platform that could operate at variable altitudes from the near surface to 10,000s of meters above it and would explore the surface and atmospheric chemistries of Titan. On either of these missions the LD-IR detection system has the potential to better analyze the surface composition than native illumination reflectance spectroscopy. On Titan, where a 1.9 µm laser can use the water absorption band, which is near in Titan's 2.0 µm atmospheric absorption window [7], a LD-IR will be able to analyze multiple samples with no complex (and costly) sample handling systems. On a comet sample return mission, as the probe approaches the surface, an LD-IR instrument could easily identify surface compositional differences, which would allow
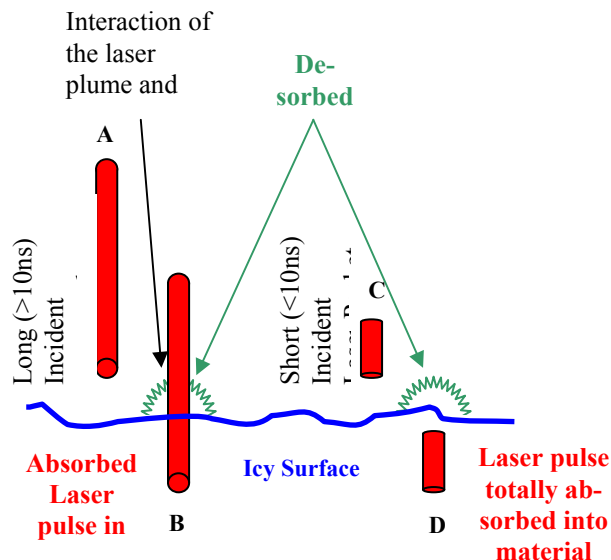

Figure 1. *A long duration photon packet is directed toward a surface (A). The initial part of the wave packet begins the desorption of surface material which then interacts with the back end of the packet (B). If the energy is large enough, the material undergoes ablation, and becomes ionized. For shorter duration packets (C), desorption occurs after the entire energy is deposited onto the sample (D) and destruction of molecular bonds is rare, ensuring a direct measurement of fragile, complex organics.*

for ground based decisions on which sample to acquire.

The current understanding of ice desorption thresholds as a function of laser frequency is incomplete [8]. This work will characterize this phenomenon in relationship to its potential future missions. Recent work indicates that the amount of energy necessary for a desorption process at ~100K using a shorter duration laser pulses at 3.1 microns is at least 6 times less than what is currently cited in the literature [8]. At this low laser fluence, LD-IR spectroscopy would not only be feasible, but would be able to be operated at power levels of missions with flight proven radioisotope power sources.

Expected signal: In order to understand a theoretical limit of detection we have calculated the emission signal of material that has been demonstrated in a laboratory setting [8,9]. A desorption plume is assumed

to have roughly the same initial diameter as the incident laser spot size. We assume that the desorption plume has a temperature of 300 K, and is traveling at a speed of 600 m/sec (as derived from Kinetic energy = $\frac{1}{2} mv^2 = 3/2 kT$). It is further assumed that the material emits at 300 K until it has traversed a distance equivalent to the spot diameter. At this point, we consider the material to have dispersed too much to provide additional signal. Both of these numbers are very conservative and should be considered worst case [9,10]. In the experiments described by [9] the spot diameter was 300 microns, giving ~5 microseconds of emission. At 300 K, the spot radiates approximately 32 microwatts, resulting in a total energy radiated of about 1.6×10^{-11}J, or about 100 MeV, which corresponds to 109 photons.
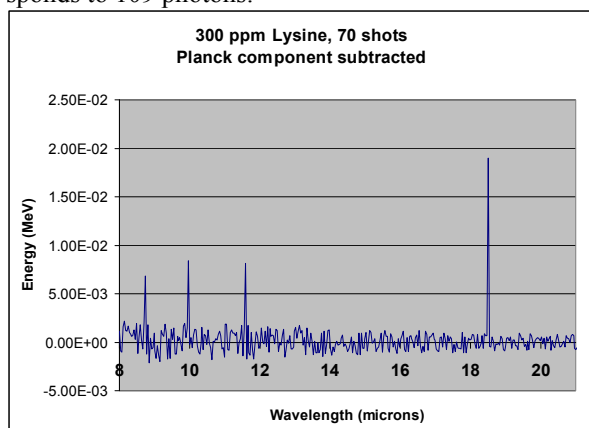
Figure 2. *Model calculations for 300 ppm Lysine, with 70 shots.*

It is assumed that the water will radiate as a Planck spectrum (i.e. the black body radiation centered at 9-10 microns). The material examined for these calculations is lysine. We chose to examine the detection of the amino acid Lysine because it is a complex organic molecule with emission line strength relative to its own Planck component which can easily be estimated from [11]. We further assume that the lysine is desorbed at the same time as the water, though this is something that must be tested. For the purposes of signal-to-noise, this assumption is once again a worst-case scenario, as the lysine emission lines must rise above the shot noise of the water spectrum. Calculations are done for multiple shots on the same location. Each laser shot will desorb approximately 0.27 microns depth of ice [9].

Multiple shots at the same location can substantially improve the detection threshold for organic contaminants in water ice. Figure 2 shows an emission spectrum, with the Planck component subtracted, for water ice with 300 ppm of Lysine, with 70 shots. Several

emission lines can be seen; the 540 cm-1 line is very prominent, and even the 1142 cm-1 line is three sigma above the shot noise. Other emission features at 1004, and 863 cm-1 are clearly visible; the 1004 and 863 cm-1lines are 4.2 sigma above the shot noise, and the 540 cm-1 line is about 18 sigma above the shot noise.

If we define the minimum detectability as occurring when the 540 cm-1 line is 3 sigma above the shot noise, then the number of shots needed for detection will be a power law in the concentration, as shown in Table 1. For concentrations of over about 400 ppm of lysine, it is anticipated that only a single shot is neces-

Table 1. *Number of laser shots to detect concentrations of Lysine.*

Lysine Concentration (ppm)	Number of shots for 3σ detection
1	17500
5	7000
10	1750
50	70
100	18
418	1

sary for a threshold detection; concentrations of less than about 50 ppm might be difficult to detect for the system modeled here, and a larger spot size may be necessary. It is anticipated that a system built on the parameters modeled here would be able to detect complex organics, like lysine, in ice to a concentration of approximately 50 ppm, without the need for sample handling and processing.

References: [1] Griffith, C. A., et al. (1997) *Icarus* 128 (2): 275-293. [2] Woodward, C. E., et al. (1998) *Earth Moon and Planets* 81 (3): 217-222. [3] Wooden, D. H., et al. (1999) *Ap J.* 517 (2): 1034-1058. [4] Wooden, D. H. (2002) *Earth Moon and Planets* 89 (1-4): 247-287. [5] Cruikshank, D. P. (2005) *Infrared/Submm Astronomy from Space* 36: 1070-1073. [6] Space Studies Board (2003) *New Frontiers in the Solar System, An Integrated Exploration Strategy.* [7] Brown, R. H., et al. (2004) *SSR* 115 (1-4): 111-168. [8] Chou, M., et al. (2004) *Space 2004 Conference.* [9] Focsa, C., et al. (2006) *Journal of Physics-Condensed Matter* 18 (30): S1357-S1387. [10] Focsa, C. personal communication. [11] Terpugov, E. L. and O. V. Degtyareva (2001). *Jetp Letters* 73 (6): 282-284.